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### (54) Novel thermoplastic elastomer composition with superior oil resistance

(57) The present invention relates to a novel thermoplastic elastomer composition with superior oil resistance along with elastomeric flexibility, creep resistance at high temperature, superior mechanical strength and moldability. The composition comprises (a) 100 parts by weight of a hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising at least

two A polymer blocks comprised mainly of a vinyl aromatic compound and at least one B polymer block comprised mainly of a conjugated diene compound; and (b) 30-300 parts by weight of a partially crosslinked thermoplastic elastomer obtained by polymerizing an acrylate monomer absorbed in a polyolefin. The novel composition can be applied as a material for various molded parts.

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**Description****Background of the Invention****5    Field of the Invention**

[0001] The present invention relates to a novel thermoplastic elastomer composition with superior oil resistance along with elastomeric flexibility, creep resistance at high temperature, superior mechanical strength and moldability. The invented composition can be applied as a material for various molded parts.

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**Background Art**

[0002] Recently, thermoplastic elastomer has been widely used in various fields such as automobile, electric appliances, wire and cables, medical goods, consumer products and footwear because it has rubber like elasticity without 15 vulcanization and can be molded just like thermoplastics.

[0003] A typical example of the thermoplastic elastomer, a block copolymer of a vinyl aromatic compound and a conjugated diene compound, such as styrene-butadiene-styrene block copolymer, however, is inferior in heat resistance, weather resistance and oil resistance, which have limited application fields.

[0004] In order to improve these properties, many compositions have been proposed such as composition between 20 hydrogenated vinyl aromatic-conjugate diene block copolymer and polyolefin as described in Japanese Laid-open Patent Application Specifications Nos. Sho 50-14742 and Sho 52-65551. These compositions have improved weather resistance and heat resistance, however, their oil resistance are still poor and equivalent to that of the above thermoplastic elastomer.

[0005] In order to improve the defect of oil resistance, a dynamic-vulcanization method with an organic peroxide for 25 a composition made of a hydrogenated block copolymer, hydrocarbon oil, polyolefin and inorganic fillers are proposed as described in Japanese Laid-open Patent Application Specifications Nos. Sho 58-13203, Sho 58-145751, Sho 59-53548, Sho 59-131613 and Sho 62-48757. These compositions have improved elasticity at high temperature, however, organic peroxide included in the composition may often cause polymer chain scission which lowers mechanical strength of the composition and oil resistance itself is not necessarily enough.

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**Summary of the Invention**

[0006] In these situations, the inventors have made extensive and intensive studies in order to develop a thermoplastic elastomer composition, which not only has superior flexibility, weather and heat resistance, low temperature 35 properties, mechanical strength, moldability typical of hydrogenated block copolymer but also exhibits excellent oil resistance. As a result, it has unexpectedly been found that, when a partially crosslinked thermoplastic elastomer composed of polyolefin and polyacrylate is blended to a hydrogenated block copolymer, the composition exhibits oil resistance equivalent to that of CR and has typical characteristics of the hydrogenated block copolymer itself.

[0007] The foregoing object, features and advantages of the present invention will be apparent to those skilled in 40 the art from the appended claims and detailed description.

[0008] According to a first embodiment, the present invention comprises a thermoplastic elastomer composition obtainable by melt blending of a compound comprising:

(a) 45 100 parts by weight of a hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising at least two A polymer blocks comprised mainly of a vinyl aromatic compound and at least one B polymer block comprised mainly of a conjugated diene compound; and  
 (b) 30-300 parts by weight of a partially crosslinked thermoplastic elastomer obtained by polymerizing an acrylate monomer absorbed in a polyolefin.

50 [0009] According to another embodiment, the invention comprises a thermoplastic elastomer composition obtainable by melt blending of a compound comprising:

(a) 55 100 parts by weight of a hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising at least two A polymer blocks comprised mainly of a vinyl aromatic compound and at least one B polymer block comprised mainly of a conjugated diene compound;  
 (b) 30-300 parts by weight of a partially crosslinked thermoplastic elastomer obtained by polymerizing an acrylate monomer absorbed in a polyolefin.  
 (c) 40-300 parts by weight of non-aromatic rubber use oil; and

(d) 5-70 parts by weight of polyolefin resin.

[0010] Preferably, in a thermoplastic elastomer composition according to the first or second embodiment above, said vinyl aromatic compound is styrene and the said conjugated diene compound is butadiene or isoprene.

5 [0011] Further, in a thermoplastic elastomer composition according to the second embodiment above, said polyolefin resin is a propylene homopolymer and/or a copolymer of propylene with ethylene or C<sub>4</sub>-C<sub>8</sub> α-olefin.

[0012] In a thermoplastic elastomer composition according to the second embodiment above, said non-aromatic rubber use oil is a oil with kinematic viscosity of 20-800 cSt at 40°C, fluidity point of 0...-40°C and flash point of 200-400°C.

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#### Detailed Description of the Invention

[0013] For easy understanding of the present invention, the essential features and various embodiments of the present invention are enumerated below.

15 [0014] Examples of a vinyl aromatic compound contained in the hydrogenated block copolymer as a (a) component include styrene, α - methylstyrene, vinyltoluene, p-tert-butylstyrene and the like. They can be used individually and in combination. Among these compounds, styrene is preferred.

20 [0015] Examples of a conjugated diene compound include butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene and the like. They can be used individually and in combination. Among these compounds, butadiene, isoprene and their combination are preferred. Microstructure of B polymer block before hydrogenation can be arbitrarily selected. For example, in the case of polybutadiene block, the content of 1,2-vinyl bond in the block is preferably from 20 to 50%, more preferably 25 to 45%. In the case of polyisoprene block, the content of 1,4 bond in the block is preferably more than 80%, more preferably more than 90%.

25 [0016] As mentioned above, the structure of the block copolymer before the hydrogenation, is comprised of at least two A polymer blocks comprised mainly of a vinyl aromatic compound and at least one B polymer block comprised mainly of a conjugated diene compound. Examples of the block structure include A-B-A, B-A-B-A, A- B-A-B-A, (A-B)<sub>4</sub>-Si, (B-A-B)<sub>4</sub>-Si, (B-A-B)<sub>4</sub>-Sn and the like.

30 [0017] The term "comprised mainly of" used herein in connection with the polymer block means that 50 % by weight or more, preferably 70 % by weight or more of all monomer units constituting the polymer block are specified monomer units which are main constituents for the respective polymer block. As examples of the remaining monomer units for each of A and B polymer blocks, there should be mentioned conjugated diene and vinyl aromatic compounds can be arranged in random, tapered, block structure or any combination of them. The term "tapered" structure means that the concentration of certain monomer units contained in the polymer block increasingly or decreasingly changes along the polymer chain. With respect to each of the polymer blocks A and B, when the number of the blocks contained before the hydrogenation is two or more, the structures of the blocks may be the same or different.

35 [0018] In the present invention, the hydrogenated block copolymer has a number average molecular weight of from 30,000 to 800,000, preferably from 50,000 to 500,000, and still more preferably from 100,000 to 400,000. When the number average molecular weight of the hydrogenated block copolymer is less than 30,000, mechanical strength and heat resistance of the thermoplastic elastomer composition are disadvantageously lowered. On the other hand, when the number average molecular weight of the hydrogenated block copolymer is more than 800,000, moldability (fluidity) of the thermoplastic elastomer composition becomes low and so surface appearance of the molded articles disadvantageously becomes poor (flow marks occur).

40 [0019] The hydrogenated block copolymer contains A blocks in an amount of from 10 to 45 % by weight, preferably from 20 to 40 % by weight. When the amount of A blocks is less than 10% by weight, mechanical strength and heat resistance of the thermoplastic elastomer composition are disadvantageously lowered. On the other hand, when the amount of A blocks is more than 45 % by weight, elastomeric flexibility and low temperature properties of the thermoplastic elastomer composition disadvantageously become poor.

45 [0020] The molecular weight distribution (MWD), which is given as a ratio of weight average molecular weight to number average molecular weight, of the hydrogenated block copolymer is preferably not more than 5, more preferably not more than 2. still more preferably not more than 1.5. When the MWD is more than 5, mechanical strength and heat resistance of the thermoplastic elastomer composition are unsatisfactory.

[0021] The molecular weight and MWD described in this invention are determined with GPC (Gel Permeation Chromatography), for example, using a calibration curve obtained with standard polystyrenes.

50 [0022] With respect to a production method of the hydrogenated block copolymer, any method can be used as long as the block structure described in this invention is obtained. For example, the desired hydrogenated block copolymer can be obtained by hydrogenating a vinyl aromatic compound conjugated diene compound block copolymer which is synthesized using a lithium catalyst in an inert medium by the method described in Japanese Published Patent Specification No. Sho 40-23798. Examples of the hydrogenation method are described such as in Japanese Published

Patents Specifications Nos. Sho 42-8704 and 43-6636 and US Patents Nos. 3,644,588 and 3,431,323.

[0023] The hydrogenation degree of the double bond of the conjugated diene compound moiety is preferably 80 % or more, more preferably 90 % or more. On the other hand, the hydrogenation degree of the double bond of the vinyl aromatic compound is preferably less than 20 %, more preferably less than 10 %. The hydrogenation degree of the obtained hydrogenated block copolymer can be easily known with infrared spectroscopy or NMR.

[0024] The production method of a partially crosslinked thermoplastic elastomer as a (b) component of this invention is described in detail in FI Patent Applications Nos. 894461, 904586, 920359, 931863, 946055, 951904 and 953803.

[0025] Examples of a polyolefin used for making component (b) include homo- or copolymer of ethylene and propylene or a blend of two or more polyolefins. A comonomer for ethylene polymer can be vinyl acetate, vinyl chloride, propylene or some other  $\alpha$ -olefin,  $C_1-C_7$ alkyl(meth)acrylate, (meth)acrylic acid, hydroxy alkyl(meth)acrylate, glycidyl(meth)acrylate, dienes such as hexadiene-1,4, hexadiene-1,5, hexadiene-1,6, 2-methyl-pentadiene-1,4, octadiene-1,7, 6-methylheptadiene-1,5, and polyenes such as octatriene and dicyclopentadiene.

[0026] Also ethylene-  $\alpha$ -olefin-polyene terpolymers can be used. Useful  $\alpha$ -olefins include propylene, butene, pentene, isoprene, hexene or their mixtures and useful polyenes include hexadiene-1,4, hexadiene-1,5, hexadiene-1,6, 2-methylpentadiene-1,4, octadiene-1,7,6-methylheptadiene-1,5,octatriene, dicyclopentadiene. In case that ethylene polymer is a copolymer, the content of ethylene must be at least 50 % by weight.

[0027] Propylene copolymers must consist over 50 % by weight propylene and can be random- or block copolymer of propylene and ethylene or also other  $\alpha$ -olefin can be used as comonomers, like dienes such as hexadiene-1,4, hexadiene-1,5, hexadiene-1,6,2-methylpentadiene-1,4,octadiene-1,7,6-methylheptadiene-1,5, and polyenes such as octatriene and dicyclopentadiene.

[0028] As functional polyolefin, polyolefin grafted with maleic acid anhydride, (meth)acrylic acid and glycidyl(meth)acrylate can be used.

[0029] Suitable acrylate monomers used for making component (b) of this invention are (meth)acrylates whose polymer have low glass transition temperature, i.e. they are rubber like at room temperature and low temperature, preferably below -20°C. Suitable acrylates are alkylacrylates having 1 or preferably 2 or more carbon atoms in the alkyl chain. Methacrylates having a glass temperature low enough are alkyl-methacrylates having 4 or more, preferably 8 or more carbon atoms in the alkyl chain. These monomers can be used alone or in mixtures of two or more monomers.

[0030] Together with the above mentioned monomers, smaller amounts of monomers having less carbon atoms in the carbon chain can also be used. Glass transition temperature of the final products can thus be tailored. According to this invention, one or more functional monomers are added to the acrylate monomer. Typical functional monomers are: glycidyl methacrylate, 2-t-butylaminoethyl methacrylate, polypropyleneglycol monomethacrylate, and mono-methacryloyloxy-ethylphthalate.

[0031] Typically, the ratio between polyacrylate and polyolefin in the component (b) is 0.1-5, preferably 0.5-2.

[0032] The amount of (b), based on 100 parts by weight of (a), in this invention is 30-300 parts by weight, preferably 50-200 parts by weight. When the amount of (b) is more than 300 parts by weight, mechanical strength and heat resistance of the thermo-plastic elastomer compound become disadvantageously lowered, although oil resistance is improved. On the other hand, when the amount of (b) is less than 30 parts by weight, oil resistance is not satisfactory.

[0033] Examples of non-aromatic oil described as a component (c) of this invention, include a non-aromatic mineral oil, such as conventional paraffinic and naphthenic oil and a liquid or low molecular weight synthetic softening agent.

[0034] Aromatic oils are not suitable because they may partially dissolve component (a) of this invention and consequently lower mechanical strength of the invented composition. Preferable examples are paraffinic oils and more preferably paraffinic oils containing less aromatic ring compounds.

[0035] The amount of a component (c) of this invention relative to 100 parts by weight of a component (a) of this invention is 40-300, preferably 80-200. When the amount is more than 300 parts by weight, the oil may bleed out, and thus giving final products stickiness and also disadvantageously lowers mechanical strength of the thermoplastic elastomer composition. On the other hand, when the amount is less than 40 parts by weight, elastic flexibility of the thermoplastic elastomer composition is not sufficient.

[0036] Examples of polyolefin described as a component (d) of this invention, include polyethylene based and polypropylene based resins.

[0037] Examples of the polyethylene based resins are LDPE, LLDPE, HDPE and copolymers of ethylene with  $C_3-C_8$   $\alpha$ -olefin such as propylene, 1-butene, isobutene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and the like. The content of the  $\alpha$ -olefin in the copolymer is preferably 30% by weight or less.

[0038] Examples of the polypropylene based resins are propylene homopolymer and random and block copolymers of propylene with ethylene and  $C_4-C_8$   $\alpha$ -olefin such as 1-butene, isobutene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene and the like. The content of the  $\alpha$ -olefin in the copolymer is preferably 30% by weight or less. These polypropylene based resins can be produced by any conventional methods such as by using Ziegler-Natta catalysts.

[0039] In order to obtain the thermoplastic elastomer composition with superior heat resistance and moldability, the polypropylene based resins are preferable as a component (d) of this invention.

[0040] Melt flow rate, (herein after referred to as MFR, measured at 230°C, 2.16 kg load as specified in ASTM D1238) of the polyolefin component (d) is 1-60 g/10 min., preferably 5-40 g/10 min. When MFR of the component (d) is less than 1 g/10 min, melt viscosity of the thermoplastic elastomer composition increase, resulting in poor moldability (fluidity) and poor surface appearance (flow marks occur) of the molded parts. On the other hand, when MFR of the component (d) is more than 60 g/10 min., mechanical strength and heat resistance of the thermoplastic elastomer composition are disadvantageously lowered.

[0041] The amount of the polyolefin component (d) of the thermoplastic elastomer composition, relative to 100 parts by weight of the component (a), is 5-60 parts by weight, preferably 10-50 parts by weight. When the amount of (d) is less than 5 parts by weight, heat resistance and moldability of the thermoplastic elastomer composition are disadvantageously lowered. On the other hand, when the amount of the component (d) is more than 60 parts by weight, elastic flexibility of the thermoplastic elastomer composition is disadvantageously lowered.

[0042] As component other than (a), (b), (c), and (d), of the thermoplastic elastomer composition of this invention, the following known additive, thermoplastic resin, elastomer and filler, depending on applications, as long as the object of the invention is satisfied.

[0043] Examples of the additives include antioxidant, heat stabilizer, light stabilizer, UV absorber, neutralizer, lubricant, antifogging agent, antiblocking agent, dispersant, colorant, flame retardant, antistatic agent, conducting filler, crosslinking agent, crosslinking co-agent, chain transfer agent, antimicrobe agent, fluorescent whitening agent and the like.

[0044] Examples of the thermoplastic resin include EVA, ethylene-(meth)acrylic acid copolymer, ethylene-(meth)acrylate copolymer, polyphenylene ether, nylon 6, nylon 66, PET, PBT, oxymethylene homo- and copolymer and the like.

[0045] Examples of the elastomer include EPM, EPDM, ethylene-butene copolymer, ethylene-propylene-butene copolymer, rubber such as SBR, SIR and PBR and the like.

[0046] Examples of the filler include glass fiber, hollow glass bead, carbon fiber, talc, calcium carbonate, mica, calcium titanate fiber, silica, titania, carbon black and the like.

[0047] In producing the thermoplastic elastomer composition of the present invention, the components for the composition can be blended by a known method. For obtaining the thermoplastic elastomer composition in the most homogeneous form, it is preferred that the above mentioned components are dry-blended, prior to melt-kneading, using a mixer, such as a Henschel mixer, a tumbler, a ribbon blender or the like, followed by melt kneading using a conventional kneader, such as a mixing roll, a kneader, a Banbury mixer, an extruder or the like.

#### Best Mode for Carrying out the Invention

[0048] Herein below, the present invention will be described in more detail with the following examples and comparative examples, which should, however, not be construed as limiting the scope of the present invention.

[0049] In the following examples and comparative examples, various properties were measured by the following methods.

(1) MFR (g/10 min.):  
ASTM D1238, at 230°C, 2.16 kg load

(2) Hardness:  
JIS K6301, A type spring, at 23°C  
Dumbbell No. 3 type test specimens are cut off from a compression molded sheet with thickness of 2 mm and four specimens are piled up for the test.

(3) Tensile Strength (MPa) and elongation at break (%):  
JIS K6301, at 23°C  
Dumbbell No. 3 type test specimens are cut off from a compression molded sheet with thickness of 2 mm.

(4) Compression Set (%):  
JIS K6301, 70°C x 22 hr. Initial compression ratio of 25%. Disk-shaped test specimens are cut off from a compression molded sheet with thickness of 2 mm and piled up to the specified thickness.

(5) Oil Resistance(%):  
JIS K6301, 70°C x 166 hr. Test specimens are cut off from a compression molded sheet with thickness of 2 mm and immersed into JIS No. one and three type oils. Weight increase and retention ratio of tensile strength were measured relative to those before the test.

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[0050] The components used in examples and comparative examples are described below.

[0051] Component (a): All of the following four components (a-1) - (a-4) were polymerized and hydrogenated by the method described in Japanese Laid-open Patent Specification No. Sho 60-220147. Their molecular structures before and after the hydrogenation are shown below:

	(a-1)	(a-2)	(a-3)	(a-4)
Block structure	A-B-A	A-B-A	A-B-A	A-B-A
A	styrene	styrene	styrene	styrene
B	BD	BD	BD	IP
	(BD=butadiene) (IP=isoprene)			
Styrene content (wt%)	33	33	30	28
1,2 and 3,4 bond (%)	35	35	35	6
Degree of Hydrogenation (%)	99	99	99	99
M <sub>n</sub> (x10,000)	16	7	25	17
MWD	1.15	1.15	1.17	1.10

[0052] Component (b) : "PACREL 631", a thermoplastic vulcanisate composed of 60% crosslinked polybutylacrylate as the dispersed phase and 40% polypropylene as the continuous phase produced by OPTATECH CORP., Finland. Density is 0.996 g/cm<sup>3</sup>, hardness 90, tensile strength 6.7MPa, elongation 86%.

[0053] Component (c) : "Diana Process Oil PW-380", paraffinic oil produced by Idemitsu Kosan Co., Ltd., Japan. Kinematic viscosity at 40°C is 382 cSt.

[0054] Component (d) : "M-1600", polypropylene produced by Japan Polyolefin Co., Ltd. MFR 15 g/10 min.

#### Examples 1-19 and comparative examples 1-5

[0055] Total components, shown in Table 1, and 0.1 parts by weight of "Irganox 1076", a phenol based stabilizer, relative to 100 parts by weight of the total components, were melt kneaded using a 45mm φ twin screw extruder at 220°C to thereby obtain pellets of the thermoplastic elastomer composition. The pellets were then compression molded at 200°C, 100 kg/cm<sup>2</sup> to furnish test pieces for the above described evaluation. The evaluation results are summarized in Tables 1 to 8.

Table 1

		Example 1	Example 2	Example 3
Weight ratio (parts by weight)	Component (a-1) Hydrogenated block copolymer	100	100	100
	Component ( b )'PACREL 631	70	135	200
	Component ( c ) Paraffinic oil	-	-	-
	Component ( d ) Polypropylene	-	-	-
Physical properties	Hardness (JIS A)	73	78	82
	MFR (g/10min)	1.5	1.8	2.1
	Tensile strength (MPa)	15.3	12.8	9.0
	Elongation at breakage (%)	400	350	310
	Compression set (%)	45	50	60
JIS NO.1 Oil Resistance	Weight increase (%)	12	8	6
	Retention of tensile strength (%)	82	90	96
JIS NO.3 Oil Resistance	Weight increase (%)	50	40	35
	Retention of tensile strength (%)	72	80	85

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Table 2

			Example 4	Example 5	Example 6
5	Weight ratio (parts by weight)	Component(a-1) Hydrogenated block copolymer	100	100	100
		Component ( b ) PACREL 631	70	70	160
		Component ( c ) Paraffinic oil	140	140	140
		Component ( d ) Polypropylene	50	30	10
10	Physical properties	Hardness (JIS A)	73	67	75
		MFR (g/10min)	5.0	3.2	2.6
		Tensile strength (MPa)	9.8	9.1	8.3
		Elongation at breakage (%)	760	800	710
		Compression set (%)	45	47	52
15	JIS NO.1 Oil Resistance	Weight increase (%)	16	18	10
		Retention of tensile strength (%)	73	70	83
20	JIS NO.3 Oil Resistance	Weight increase (%)	58	65	48
		Retention of tensile strength (%)	56	52	65

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Table 3

			Example 7	Example 8	Example 9
30	Weight ratio (parts by weight)	Component(a-1) Hydrogenated block copolymer	100	100	100
		Component ( b ) PACREL 631	160	160	160
		Component ( c ) Paraffinic oil	140	140	80
		Component ( d ) Polypropylene	30	50	30
35	Physical properties	Hardness (JIS A)	78	82	85
		MFR (g/10min)	4.0	4.5	3.2
		Tensile strength (MPa)	10.5	12.6	13.9
		Elongation at breakage (%)	640	650	630
		Compression set (%)	53	58	58
40	JIS NO.1 Oil Resistance	Weight increase (%)	7	8	7
		Retention of tensile strength (%)	85	92	88
45	JIS NO.3 Oil Resistance	Weight increase (%)	45	41	49
		Retention of tensile strength (%)	55	69	53

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Table 4

		Example 10	Example 11	Example 12
5	Weight ratio (parts by weight)	Component(a-1) Hydrogenated block copolymer	100	100
		Component ( b ) PACREL 631	160	240
		Component ( c ) Paraffinic oil	200	120
		Component ( d ) Polypropylene	30	20
10	Physical properties	Hardness (JIS A)	68	80
		MFR (g/10min)	6.0	3.5
		Tensile strength (MPa)	8.9	6.0
		Elongation at breakage (%)	700	690
		Compression set (%)	55	63
15	JIS NO.1 Oil Resistance	Weight increase (%)	11	85
		Retention of tensile strength (%)	75	86
20	JIS NO.3 Oil Resistance	Weight increase (%)	43	35
		Retention of tensile strength (%)	58	69
				72

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Table 5

		Example 13	Example 14	Example 15
30	Weight ratio (parts by weight)	Component(a) Hydrogenated block copolymer	(a-1) 100	(a-2) 100
		Component ( b ) PACREL 631	240	135
		Component ( c ) Paraffinic oil	200	-
		Component ( d ) Polypropylene	20	-
35	Physical properties	Hardness (JIS A)	74	75
		MFR (g/10min)	5.0	3.0
		Tensile strength (MPa)	5.3	9.0
		Elongation at breakage (%)	680	300
		Compression set (%)	67	67
40	JIS NO.1 Oil Resistance	Weight increase (%)	11	18
		Retention of tensile strength (%)	84	65
45	JIS NO.3 Oil Resistance	Weight increase (%)	45	58
		Retention of tensile strength (%)	63	51
				88

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Table 6

			Example 16	Example 17	Example 18
5	Weight ratio (parts by weight)	Component(a) Hydrogenated block copolymer	(a-4) 100	(a-2) 100	(a-3) 100
		Component ( b ) PACREL 631	135	160	160
		Component ( c ) Paraffinic oil	-	140	140
		Component ( d ) Polypropylene	-	30	30
10	Physical properties	Hardness (JIS A)	78	74	80
		MFR (g/10min)	1.6	7.0	2.5
		Tensile strength (MPa)	10.0	5.9	13.6
		Elongation at breakage (%)	310	650	750
		Compression set	55	66	47
15	JIS NO.1 Oil Resistance	Weight increase (%)	15	19	7
		Retention of tensile strength (%)	72	62	95
20	JIS NO.3 Oil Resistance	Weight increase (%)	48	62	38
		Retention of tensile strength (%)	69	52	75

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Table 7

		Example 19
30	Weight ratio (parts by weight)	Component ( a ) Hydrogenated block copolymer (a-4) 100
		Component ( b ) PACREL 631 160
		Component ( c ) Paraffinic oil 140
		Component ( d ) Polypropylene 30
35	Physical properties	Hardness (JIS A) 79
		MFR (g/10min) 3.7
		Tensile strength (MPa) 8.8
		Elongation at breakage (%) 610
		Compression set (%) 56
40	JIS NO.1 Oil Resistance	Weight increase (%) 13
		Retention of tensile strength (%) 70
45	JIS NO.3 Oil Resistance	Weight increase (%) 57
		Retention of tensile strength (%) 50

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Table 8

		Comparative Example 1	Comparative Example 2	
5	Weight ratio (parts by weight)	Component(a-1) Hydrogenated block copolymer	100	
	Component ( b ) PACREL 631	-	350	
	Component ( c ) Paraffinic oil	140	140	
	Component ( d ) Polypropylene	30	30	
10	Physical properties	Hardness (JIS A)	57	
		MFR (g/10min)	3.0	
		Tensile strength (MPa)	15.0	
		Elongation at breakage (%)	900	
		Compression set (%)	42	
15	JIS NO.1 Oil Resistance	Weight increase (%)	60	
		Retention of tensile strength (%)	45	
	JIS NO.3 Oil Resistance	Weight increase (%)	200	
		Retention of tensile strength (%)	-	
20			84	
25				
30				

Industrial Applicability

[0056] The thermoplastic elastomer composition of this invention has superior oil resistance along with practically enough level of mechanical strength, heat resistance and moldability. Therefore it is useful in various fields including automobile parts .

**Claims**

- 40 1. A thermoplastic elastomer composition, characterized in that it is obtainable by melt blending of a compound comprising:
  - (a) 100 parts by weight of a hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising at least two A polymer blocks comprised mainly of a vinyl aromatic compound and at least one B polymer block comprised mainly of a conjugated diene compound; and
  - (b) 30-300 parts by weight of a partially crosslinked thermoplastic elastomer obtained by polymerizing an acrylate monomer absorbed in a polyolefin.
- 45 2. A thermoplastic elastomer composition, characterized in that it is obtainable by melt blending of a compound comprising:
  - (a) 100 parts by weight of a hydrogenated block copolymer obtained by hydrogenating a block copolymer comprising at least two A polymer blocks comprised mainly of a vinyl aromatic compound and at least one B polymer block comprised mainly of a conjugated diene compound;
  - (b) 30-300 parts by weight of a partially crosslinked thermoplastic elastomer obtained by polymerizing an acrylate monomer absorbed in a polyolefin.
  - (c) 40-300 parts by weight of non-aromatic rubber use oil; and

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(d) 5-70 parts by weight of polyolefin resin.

3. The thermoplastic elastomer composition according to claims 1 and 2, wherein said vinyl aromatic compound is styrene and said conjugated diene compound is butadiene or isoprene.  
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4. The thermoplastic elastomer composition according to claim 2, wherein said polyolefin resin is a propylene homopolymer and/or a copolymer of propylene with ethylene or C<sub>4</sub>-C<sub>8</sub> α-olefin.
- 10 5. The thermoplastic elastomer composition according to claim 2, wherein said non-aromatic rubber use oil is a oil with dynamic viscosity at 40°C of 20-800cSt, fluidity point of 0...-40°C and flash point of 200-400°C.

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## EUROPEAN SEARCH REPORT

Application Number  
EP 98 66 0048

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
P, X	EP 0 810 262 A (RIKEN VINYL IND) 3 December 1997 * page 5, line 18-21 ; page 8, line 31-49; page 7, line 1- page 8, line 8 ; page 9, line 44-52 * * page 4, line 25-50 * ---	1-5	C08L53/02 C08L23/02
X	EP 0 765 914 A (MITSUBISHI CHEM CORP) 2 April 1997 * page 6, line 36 ; page 6, line 34-46 ; page 9, line 56-57 ; page 4, line 12-13 * * page 3, line 58 * ---	1	
X	EP 0 520 515 A (FURUKAWA ELECTRIC CO LTD) 30 December 1992 * page 4, line 57 - page 5, line 11 * * page 6, line 16-18 * ---	1	
Y	EP 0 770 645 A (RIKEN VINYL IND) 2 May 1997 * page 8, line 37 ; page 9, line 12 - 20 * * page 3, line 58 - page 5, line 58 * ---	1-5	TECHNICAL FIELDS SEARCHED (Int.Cl.6)
Y	GB 2 210 047 A (EVODE LTD) 1 June 1989 * the whole document * ---	1-5	C08L
A	PATENT ABSTRACTS OF JAPAN vol. 095, no. 008, 29 September 1995 & JP 07 138418 A (RIKEN VINYL KOGYO KK; OTHERS: 01), 30 May 1995 * abstract * -----	1-5	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	2 February 1999	Hammond, A	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 66 0048

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

02-02-1999

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0810262 A	03-12-1997	JP 9316285 A JP 10310617 A	09-12-1997 24-11-1998
EP 0765914 A	02-04-1997	JP 7316416 A US 5717014 A WO 9532244 A	05-12-1995 10-02-1998 30-11-1995
EP 0520515 A	30-12-1992	JP 5263048 A DE 69206331 D DE 69206331 T US 5538771 A JP 5320587 A JP 5125338 A	12-10-1993 11-01-1996 29-08-1996 23-07-1996 03-12-1993 21-05-1993
EP 0770645 A	02-05-1997	JP 8225713 A JP 9151295 A JP 9278979 A	03-09-1996 10-06-1997 28-10-1997
GB 2210047 A	01-06-1989	NONE	